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Sampling of Technetium-99 in  
Vegetation and Soils in the  
Vicinity of Operating Gaseous  
Diffusion Facilities

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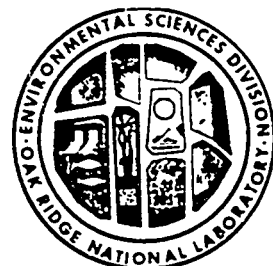
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IN THE VICINITY OF OPERATING GASEOUS DIFFUSION FACILITIES<sup>1</sup>

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## ABSTRACT

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Technetium-99 was measured in vegetation and soils collected near three operating gaseous diffusion facilities to obtain estimates of the soil-to-vegetation concentration factor. Analyses were performed primarily using radiochemical separations and low-level beta counting techniques with selected samples checked by isotope dilution mass spectroscopy. The concentration factor pooled from all three facilities appeared to be lognormally distributed with a geometric mean of 9.5 and a geometric standard deviation of 2.4. These values are comparable to calculated equilibrium concentration factors derived from other field experiments in which concentrations in soil and vegetation were observed to decrease with time subsequent to a single application of  $^{95m}\text{TcO}_4^-$ . These field values are one to two orders of magnitude less than concentration factors derived from laboratory experiments using potted plants. It is suggested that the radiological significance of  $^{99}\text{Tc}$  in terrestrial food chains of importance to humans may be substantially lower than indicated by the simple difference between laboratory and field concentration factors if the time dependency of technetium activity in vegetation and soil is taken into consideration in radiological assessment models.



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## 1. INTRODUCTION

Technetium-99 (beta energy = 0.292 MeV and radioactive half-life =  $2.1 \times 10^5$  years) is a major fission product contained within recycled uranium fuel. Until relatively recently, virtually no data were available in the literature on the uptake of technetium (Tc) by plants or the behavior of technetium compounds in soils. This lack of information is partly due to the fact that low levels of naturally occurring technetium isotopes are difficult to detect, and that environmental contamination from  $^{99}\text{Tc}$  in weapons fallout has received only limited attention. In lieu of information about technetium in soils and vegetation, Ng et al. (1968) relied upon a series of assumptions which related the behavior of technetium in the environment to that of iodine. These assumptions enabled them to derive a soil-to-plant concentration factor of 1.0 (Bq/kg dry wt plant tissue per Bq/kg dry wt soil). This value, converted to 0.25 by assuming that 25% of the fresh weight of plant tissue is dry matter, is the soil-to-plant concentration factor for technetium that has been adopted throughout the assessment literature (Baker et al. 1976, Killough and McKay 1976, USNRC 1977).

In 1974, Gast (1975) began to study Tc absorption by soils and Tc uptake by plants. Plants grown in soils watered with a solution containing  $^{99}\text{Tc}$  pertechnetate ( $\text{TcO}_4^-$ ) showed appreciable uptake and translocation of  $^{99}\text{Tc}$  into aboveground tissue, with concentrations in seeds being much less than those in foliar tissue. The observed soil-to-plant concentration factors were as much as three orders of magnitude greater than the assumed value of 0.25 (or 1.0 on a dry wt basis). Table 1 lists the soil-to-plant concentration factors reported on a dry weight basis by Gast et al. (1976).

However, in these laboratory experiments no effort was made to achieve an equilibrium level of  $^{99}\text{Tc}$  between soil and plant tissue. The plants in these experiments did not reach maturity prior to sampling. Furthermore, the concentration at which the  $^{99}\text{Tc}$  was applied was significantly higher than that which one would expect to

Table 1. Concentration factors for  $^{99}\text{Tc}$  based upon soil-to-aerial parts of wheat seedlings (Bq/kg dry wt of plant per Bq/kg dry wt of soil) from laboratory pot experiments (Gast et al. 1976)

Soil series <sup>a</sup>	Concentration factor			
	Soils watered with solution containing $^{99}\text{Tc}^b$		Soils moist-incubated with $^{99}\text{Tc}^b$	
	Unfertilized	Fertilized	Unfertilized	Fertilized
Bearden	830	460	970	95
Hegne	1120	760	710	190
Hibbing	925	715	1490	350
Nicollet (surface)	1200	875	1275	705
Nicollet (subsurface)	1065	995	1310	1305
Omega	655	445	295	235
Bergland	955	800	720	505
Arveson	685	250	525	350
Waukegan	1160	875	1170	885
Zimmerman	1055	825	805	595
(Sapric peat)	590	660	715	860

<sup>a</sup>The soils are representative of the range of pH, organic matter content, and texture found in Minnesota.

<sup>b</sup>A total of 6  $\mu\text{Ci}$  ( $2.2 \times 10^5$  Bq) of  $^{99}\text{Tc}$  was applied to the soil of each pot in which four seedlings were growing.

find in the environment around a nuclear installation, and it was sufficiently high that plant toxicity was observed. Cataldo et al. (1977) reported that the uptake of technetium by plants may be affected by the concentration of technetium in soil; there is a greater rate of uptake at higher concentrations. These laboratory data, therefore, do not provide an estimate of Tc uptake by plants in the environment around a nuclear facility, where soils could contain low levels of contamination as a result of routine releases of  $^{99}\text{Tc}$ .

Soil-to-leaf concentration factors for wheat and soybean plants that were derived from data published by Wildung et al. (1975, 1977) are listed in Table 2. Routson and Cataldo (1978) and Cataldo (1979) also recently reported similar concentration factors for  $^{99}\text{Tc}$  uptake into cheatgrass and tumbleweed grown in surface and subsurface soils. As with the experiments reported by Gast et al. (1976), the level of  $^{99}\text{Tc}$  in laboratory soil was achieved through a single application of the isotope and therefore concentration factors listed in Table 2 may not be representative of what would be expected under chronic release conditions.

Additional data were obtained on  $^{99}\text{Tc}$  uptake by Thorvig (1977). Wheat plants were germinated and grown for 10 d in 1900 ml of  $^{99}\text{Tc}$ -labelled, one-third strength Hoagland solution at three concentration levels (0.026, 0.264, and 1.057 g/ml), each of which was maintained constant ( $\pm 10\%$ ). The resulting solution/plant concentration factors were 435, 400, and 338 (Bq/kg dry tissue per Bq/liter solution), respectively, for the three concentration levels. Similar results have been given for a variety of food crops in a recent summary report issued by Gast et al. (1979).

It is of interest to note that an absolute maximum soil-to-plant concentration factor for  $^{99}\text{Tc}$  (or any other isotope for which specific data were not available) was assumed to be 100 (Bq/kg dry wt tissue per Bq/kg dry wt soil) by Ng et al. (1968). This assumption was used by Ng et al. to derive conservative values for technetium concentrations in beef and in the total body of adult humans to compensate for the absence of experimental data on the long-term retention of this element in humans and other large mammals.

Table 2. Concentration factors for  $^{99}\text{Tc}$  based upon soil-to-aerial parts of soybean and wheat (Bq/kg dry wt of plant tissue per Bq/kg dry wt of soil) derived from laboratory pot experiments (Wildung et al. 1975, 1977)

Concentration of Tc ( $\mu\text{g Tc/g soil}$ ) <sup>a</sup>	Concentration factor	
	Soybeans <sup>b</sup>	Wheat <sup>b</sup>
0.001	380	340
0.01	140	150
0.1	67	170
1.0	380	No growth
5.0	76	No growth

<sup>a</sup>Ritzville silt loam.

<sup>b</sup>Harvested 30 d after emergence.



To examine the potential significance of soil-to-plant concentration factors derived from laboratory pot experiments, Till et al. (1979) assumed a value equivalent to 200 (Bq/kg dry wt plant tissue per Bq/kg dry wt soil).<sup>\*</sup> They then used this value in the terrestrial food chain model given in Regulatory Guide 1.109 (USNRC 1977) to estimate the dose to humans resulting from releases of <sup>99</sup>Tc to the atmosphere, although they recognized that a value based on potted plant experiments might not be relevant to conditions in the field. The absence of pertinent data precluded justification of an alternative.

The dose assessment performed by Till et al. predicted that a continuous release of 1 Ci ( $3.7 \times 10^{10}$  Bq) per year of <sup>99</sup>Tc from a height of 20 m would, at a downwind distance of 1600 m (1 mile), accumulate approximately 25 Bq/kg in the 0- to 15-cm root zone of soil, after a release period of 15 years. The soil concentration, when multiplied by the dry weight soil-to-plant concentration factor of 200, produced a calculated concentration in vegetation of 5000 Bq/kg dry wt plant tissue. An adult individual assumed to ingest vegetables, meat and milk produced at this location was estimated to receive a maximum annual dose of 18 mrem ( $1.8 \times 10^{-4}$  Sv) to the G. I. tract and 80 mrem ( $8.0 \times 10^{-4}$  Sv) to the thyroid. These calculated doses approach and exceed, respectively, the Uranium Fuel Cycle Standards promulgated by the U.S. Environmental Protection Agency of 25 mrem ( $2.5 \times 10^{-4}$  Sv) to all organs of the human body except the thyroid and 75 mrem ( $7.5 \times 10^{-4}$  Sv) to the thyroid. According to Till et al., releases of <sup>99</sup>Tc to the atmosphere on the order of 1 Ci ( $3.7 \times 10^{10}$  Bq) per year is comparable to reported releases for operating gaseous diffusion facilities handling reprocessed fuels. Therefore, an investigation of the actual behavior of <sup>99</sup>Tc in soils and vegetation in the environs of these facilities is in order to test the relevancy of soil-to-plant concentration factors obtained from laboratory experiments.

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<sup>\*</sup>The value of 200 is derived from the value of 50 (dpm/g wet wt plant tissue per dpm/g dry wt soil) used by Till et al. (1979) assuming that only 25% of fresh plant tissue is dry matter.

The objective of this study was to measure the concentration of  $^{99}\text{Tc}$  in soils and vegetation at selected sites surrounding the three operating gaseous diffusion plants in the United States: Oak Ridge Gaseous Diffusion Plant, Oak Ridge, Tennessee; Paducah Gaseous Diffusion Plant, Paducah, Kentucky; and Portsmouth Gaseous Diffusion Plant, Portsmouth, Ohio. The ratio of measured plant and soil concentrations (plant/soil) constitutes the soil-to-plant concentration factor. No method was available to directly distinguish between that portion of  $^{99}\text{Tc}$  in the leaves of the sampled vegetation which resulted from direct atmospheric deposition and that which resulted from root uptake of  $^{99}\text{Tc}$  deposited in the soil, although if the high concentration factors observed from laboratory data are relevant, less than 1% of the concentration in the leaves of vegetation would be due to direct deposition (Till et al. 1979). This report is a documentation of the vegetation and soil concentrations and related concentration factors observed in the environs of the three gaseous diffusion plants. It does not constitute an analysis of the environmental impact of  $^{99}\text{Tc}$  in the vicinity of these facilities, as such an analysis would have to be based on the results of specific environmental monitoring programs designed to determine the concentrations of  $^{99}\text{Tc}$  in air, water, and foods at locations actually utilized by members of the general public.

## 2. METHODS

### 2.1 Field Vegetation and Soil Sampling Procedures

Because of the recognized difficulty in detecting low levels of  $^{99}\text{Tc}$  in environmental samples, sites were selected just outside the perimeter fence of each gaseous diffusion plant to enhance the probability of collecting detectable quantities of technetium. The herbaceous vegetation at each site was dominated by Festuca sp. (fescue grass). These sites were located approximately in the predominant wind direction from estimated sources of release (Figs. 1, 2, and 3). The wind rose diagrams in these figures depict the direction in which the wind is blowing. The approximate distance from the source of release to the sampling sites is estimated to vary between 800 and 1600 m. All of these sites are located within the area controlled by the U.S. Department of Energy. The first sampling of vegetation and soils involved collection of above-ground vegetation by hand and collection of large quantities of soil using a shovel to obtain a sample representative of the root zone (0-15 cm). All samples were placed in plastic bags and transported to Oak Ridge National Laboratory where they were dried, prepared, and analyzed for  $^{99}\text{Tc}$ .

Concurrent experimental field research conducted at Oak Ridge National Laboratory (Hoffman et al. in preparation) indicated that initially, most of the deposited technetium (deposited as  $^{95\text{m}}\text{TcO}_4^-$ ) would be found in the top 2 cm of soil. Therefore, subsequent samplings of soil in the vicinity of the gaseous diffusion plants were differentiated between 0-2 cm and below 2 cm. The maximum depth of soil sampling varied between 10 and 15 cm, depending on the rock content of soil. In addition to analysis for  $^{99}\text{Tc}$ , soils were also analyzed for pH (in 0.01 M  $\text{CaCl}_2$  solutions) and organic matter content (weight loss on ignition for 8 or more hours at 450 C) to search for any potential correlations with  $^{99}\text{Tc}$  uptake by plants. Specific aspects of sampling at each facility are discussed below.

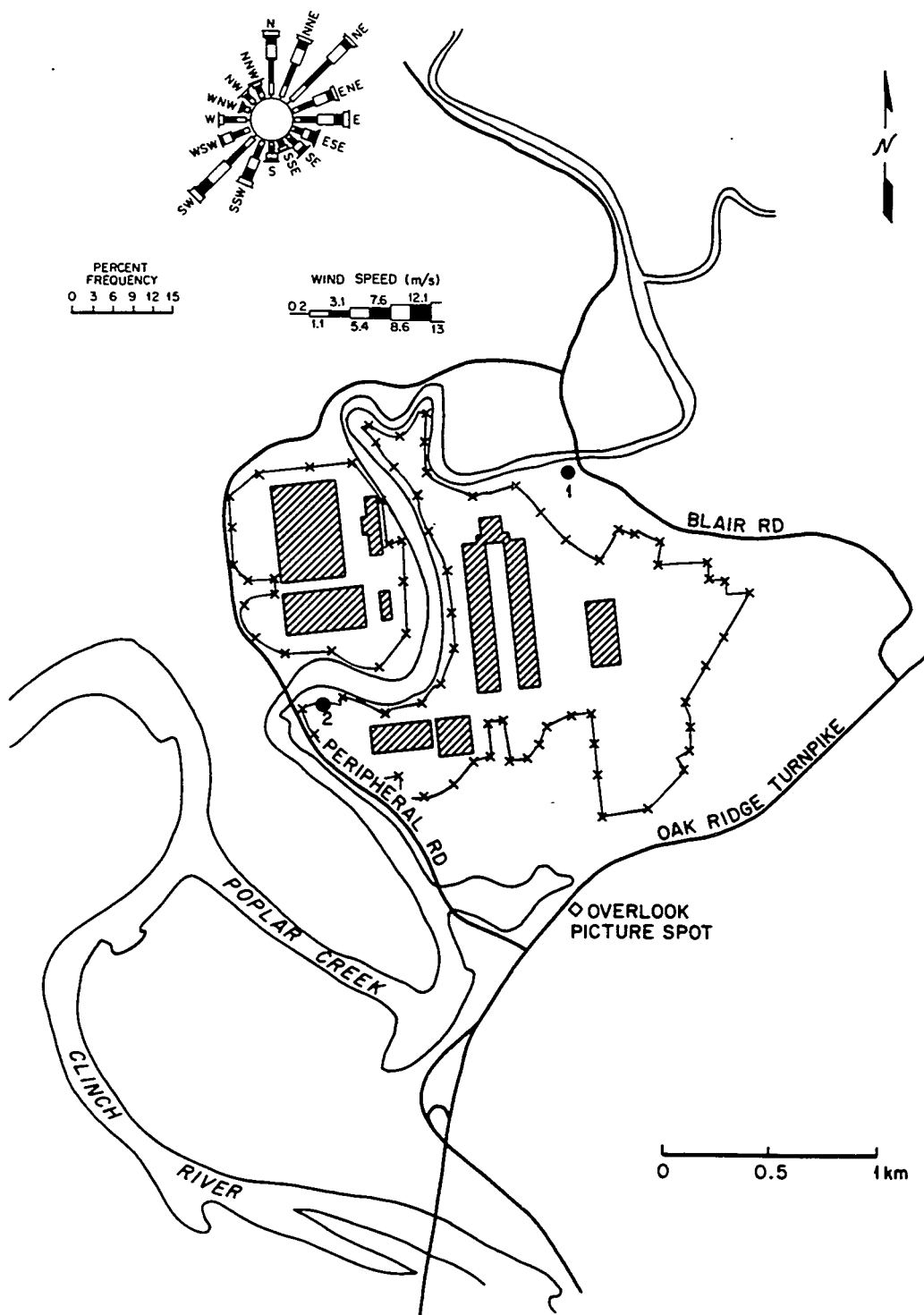


Fig. 1. Sampling locations for Oak Ridge Gaseous Diffusion Plant (sampling sites are indicated by numbered dots, x-x-x indicates the location of the peripheral fence, and the windrose indicates the direction in which the wind is blowing).

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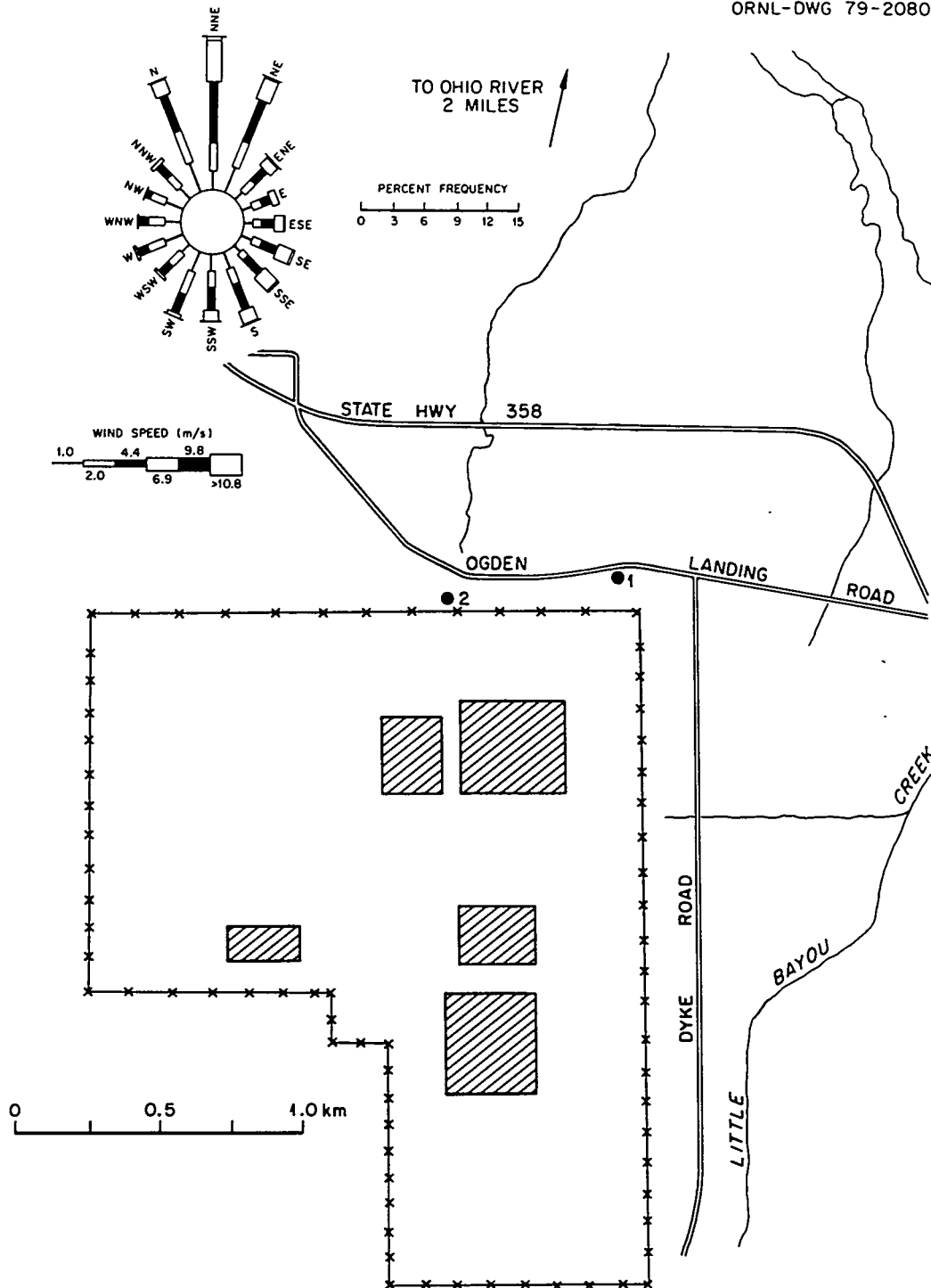


Fig. 2. Sampling locations for Paducah Gaseous Diffusion Plant (sampling sites are indicated by numbered dots, x-x-x indicates the location of the peripheral fence, and the windrose indicates the direction in which the wind is blowing).

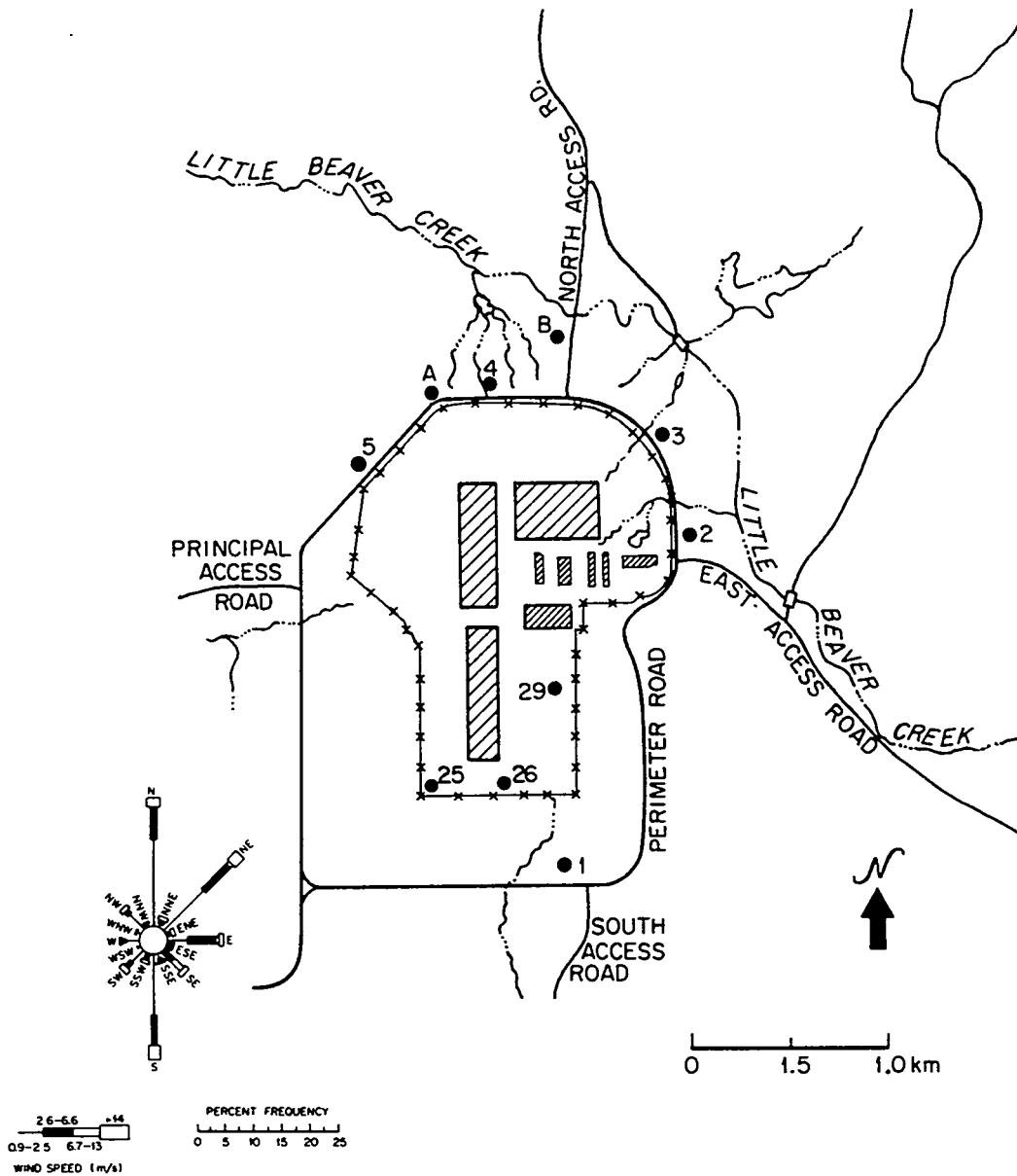


Fig. 3. Sampling locations for Portsmouth Gaseous Diffusion Plant (sampling sites are indicated by numbered dots, x-x-x indicates the location of the peripheral fence, and the windrose indicates the direction in which the wind is blowing).

### 2.1.1 Oak Ridge Gaseous Diffusion Plant

The two locations at which vegetation and soils were collected near the Oak Ridge Gaseous Diffusion Plant are depicted in Fig. 1. At sampling location No. 1, the soil type was Dewey silt loam. At sampling location No. 2, the soil type was Sequatchie very fine sandy loam. On July 14 and November 10, 1978, multiple samples of vegetation and soils were pooled into one large sample representative of each location. The approximate area over which samples were taken was 2500 m<sup>2</sup>. On July 5, 1979, samples were taken from three sites within each sampling location, and estimates were made of the standing crop biomass (g/m<sup>2</sup>) of vegetation. The area over which samples were taken at each of these sites was approximately 400 m<sup>2</sup>. Soils sampled prior to November 10, 1978, were not differentiated between the 0- to 2-cm and below 2-cm depths.

### 2.1.2 Paducah Gaseous Diffusion Plant

The two locations at which vegetation and soils were collected near the Paducah Gaseous Diffusion Plant are depicted in Fig. 2. Soils at both of these locations are of the Henry silt loam formation. On July 20 and October 23, 1978, multiple samples of vegetation and soils were pooled into one large sample representative of each sampling location. The approximate area over which samples were taken was 2500 m<sup>2</sup>. On August 21, 1979, samples were taken from three sites within each sampling location, and estimates were made of the standing crop biomass (g/m<sup>2</sup>) of vegetation. The area over which samples were taken at each of these sites was approximately 400 m<sup>2</sup>. Soils were not differentiated between the 0 to 2-cm and below 2-cm depths for samples taken prior to October 23, 1978. Because of the extent of the rock content of the soil in the locations sampled at Paducah, the maximum sample depth did not exceed 10 cm.

### 2.1.3 Portsmouth Gaseous Diffusion Plant

The ten locations at which vegetation and soils were collected near the Portsmouth Gaseous Diffusion Plant are depicted in Fig. 3. All of the soils collected from these locations belong to the

Monongahela-Philo-Tyler formation. For the first series of sampling on October 31, 1978, only two sites (A and B) were selected. Because of difficulties in detecting significant quantities of  $^{99}\text{Tc}$  in vegetation, the sampling regime was expanded on April 5, 1979, to include locations 1 through 5 along the periphery of the perimeter fence. At each location multiple samples were pooled to form one large sample representative of the site. Samples at each location were taken over an area of approximately  $2500\text{ m}^2$ . On September 7, 1979, samples were collected by the staff of Goodyear Atomic Corporation inside the perimeter fence at locations 25, 26, and 29. These samples were collected because of difficulties in detecting  $^{99}\text{Tc}$  in previous samples of vegetation (and access to Portsmouth Gaseous Diffusion Plant during September 1979 was untimely because of a union strike). Five subsamples of vegetation obtained from location 25 and three subsamples each from locations 26 and 29 were prepared for analysis of  $^{99}\text{Tc}$  at Oak Ridge National Laboratory. Two subsamples of soil from the samples obtained from all three locations were also prepared for analysis. Unlike the initial sampling at the Oak Ridge and Paducah Gaseous Diffusion Plants, the soils sampled at Portsmouth were all separated into a sample collected at the 0 to 2-cm depth and a sample collected at the below 2-cm soil depth.

## 2.2 Chemical Analysis

The two types of materials (soil and vegetation) analyzed in this study were handled differently in preparation for the radiochemical separation of  $^{99}\text{Tc}$  (Appendix A). Duplicates of both materials were processed for each sample, and one portion of each sample was spiked with  $^{95\text{m}}\text{Tc}$  which was used as a tracer to determine chemical recovery.

Soil samples were dried, milled, sieved, and leached with sodium hypochlorite and hydrogen peroxide to bring the  $^{99}\text{Tc}$  into solution (Appendix B). The solutions were made to volume, and duplicate aliquots were taken with one aliquot being spiked with  $^{95\text{m}}\text{Tc}$ . The vegetation samples were dried and milled and duplicate portions taken for analysis with one portion being spiked with  $^{95\text{m}}\text{Tc}$ . Both test



portions of the vegetation samples were saturated with ammonium hydroxide, redried, charred, and ashed at 500 C. This procedure resulted in less than 3% loss of technetium due to volatilization. The ashed material was fused with potassium carbonate and then dissolved in water.

After the materials were prepared for analysis, the same radiochemical separation scheme was used for both materials to chemically isolate and purify Tc as outlined in Fig. 4. The scheme involved the extraction of  $\text{TcO}_4^-$  from a basic aqueous solution with methyl ethyl ketone, evaporation of the ketone extract over water, and the precipitation of hydroxides from the water to remove other radioelements. The water containing the Tc isotopes was extracted with methyl ethyl ketone which was then evaporated over another portion of water. The unspiked sample was dried on a counting disc and counted on a low-background counter for the determination of  $^{99}\text{Tc}$  beta activity. Yield determinations were made by evaluating the  $^{95\text{m}}\text{Tc}$  recovery in the spiked sample by gamma-ray spectrometry and assuming that the recovery for the unspiked sample was identical to the spiked one. After the  $^{99}\text{Tc}$  concentrations were determined by beta counting, several samples of various concentrations were selected to be analyzed by isotope dilution mass spectrometry to validate the results.

Special preparations were performed for the mass spectrometry analysis. The samples containing the  $^{95\text{m}}\text{Tc}$  spikes were spiked with  $^{97}\text{Tc}$ , and all of the Tc isotopes were adsorbed on four 0.3-mm anion resin beads. The beads were subsequently sent to the mass spectrometry laboratory for analysis (Appendix C).

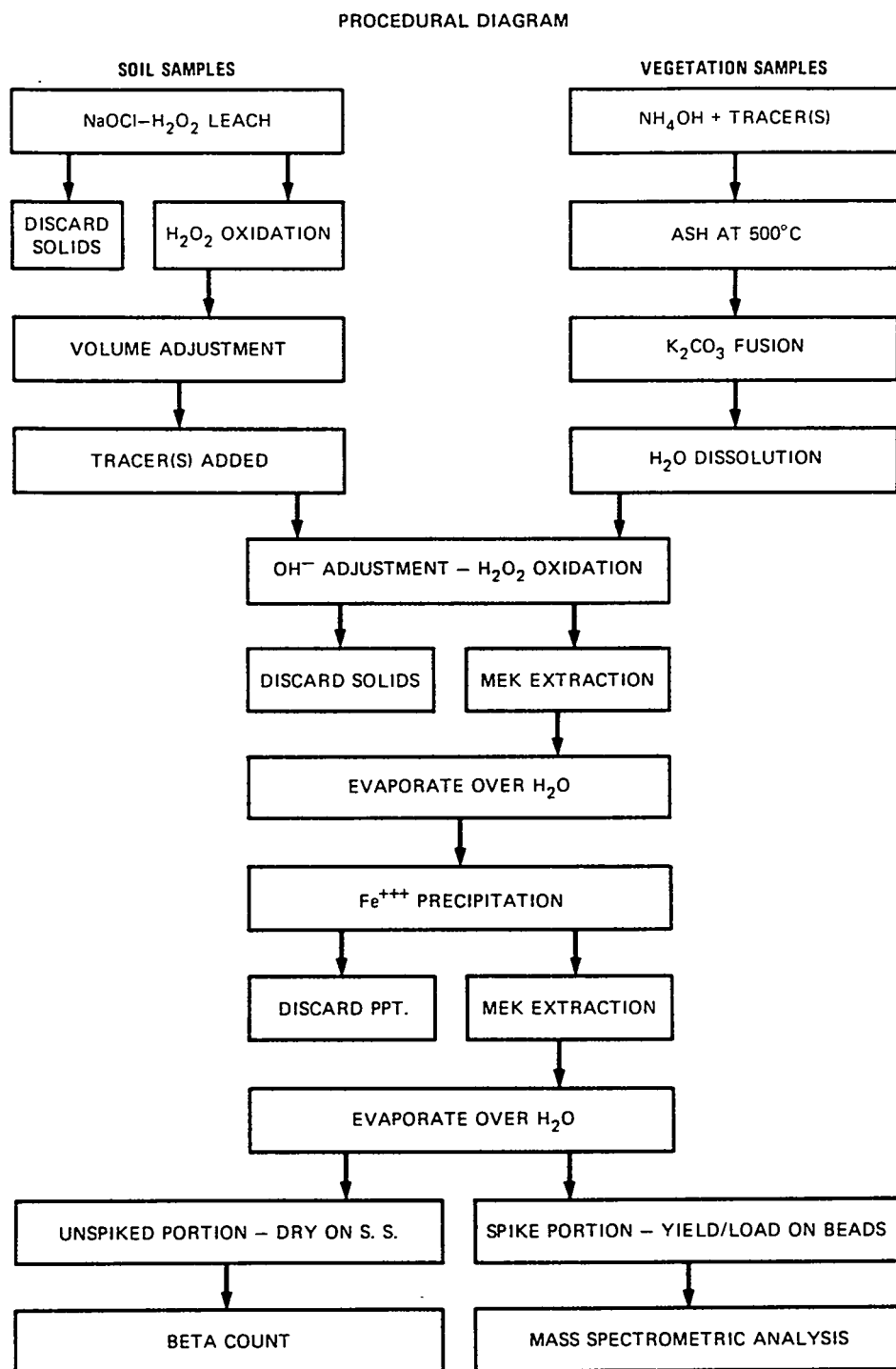


Fig. 4. Radiochemical and mass spectrometric procedures for analysis of  $^{99}\text{Tc}$ .

### 3. RESULTS

#### 3.1 Concentrations of Technetium-99 in Vegetation and Soils

The concentrations in vegetation and soil listed in Tables 3 through 5 were determined by radiochemical analysis. Selected samples reanalyzed with isotope dilution mass spectrometry to test for possible error in the radiochemical techniques confirmed the accuracy of these values. A comparison of samples analyzed with radiochemical techniques and isotope dilution mass spectrometry is given in Table 6. The estimated concentration in soil due to global fallout of  $^{99}\text{Tc}$  from nuclear weapons tests is  $6 \times 10^{-3}$  Bq/kg (Wildung et al. 1979).

##### 3.1.1 Oak Ridge Gaseous Diffusion Plant

The concentrations of  $^{99}\text{Tc}$  in vegetation sampled near the Oak Ridge Gaseous Diffusion Plant range from 42 to 84 Bq/kg dry wt at sampling location No. 1 and from 35 to 200 Bq/kg dry wt at sampling location No. 2. The geometric mean value of all vegetation concentrations is 74 Bq/kg with a geometric standard deviation of 1.8. The soil concentrations range from 5.0 to 30 Bq/kg in the top 2-cm samples and from 3 to 12 Bq/kg in the below 2-cm samples taken from location No. 1. For sampling location No. 2 the soil concentrations in the top 2-cm range from 15 to 62 Bq/kg and from 3 to 23 Bq/kg in the below 2-cm samples. The geometric mean for all soil samples taken at the 0 to 2-cm depth is 19 Bq/kg with a geometric standard deviation of 2.3. At the below 2-cm depth, the geometric mean for all soil samples is 7.3 Bq/kg with a geometric standard deviation of 2.0.

The concentrations per gram vegetation sampled on July 5, 1979, are equivalent to a geometric mean of the inventory of activity in vegetation of 11 and 12 Bq/m<sup>2</sup> for sampling locations No. 1 and No. 2, respectively, when account is taken for the estimated standing crop biomass of each sample site (plant  $^{99}\text{Tc}$  inventory = biomass x concentration). The concentrations of  $^{99}\text{Tc}$  detected for each sample collected in the vicinity of Oak Ridge Gaseous Diffusion Plant

Table 3. Concentrations of  $^{99}\text{Tc}$  in vegetation and soils in the vicinity of Oak Ridge Gaseous Diffusion Plant

Concentrations (Bq/kg dry wt)						Location	Date of collection
Vegetation	Soil <sup>a</sup>	Soil (0-2 cm)	Soil <sup>b</sup> (below 2 cm)	Biomass (kg • dry wt/m <sup>2</sup> )	Plant inventory (Bq/m <sup>2</sup> )		
< 80	< 20	-	-	-	-	No. 1	7/14/78
200	< 80	-	-	-	-	No. 2	7/14/78
84 ± 30 <sup>c</sup>		14 ± 2	7.3 ± 1	-	-	No. 1	11/10/78
150 ± 30		47 ± 3	8.9 ± 1.5	-	-	No. 2	11/10/78
67 ± 7 <sup>d</sup>		30 ± 3	12 ± 2	0.31	21	No. 1a	7/5/79
42 ± 5		10 ± 2	10 ± 2	0.19	8	No. 1b	7/5/79
53 ± 5		15 ± 2	5 ± 2	0.14	4.9	No. 2a	7/5/79
52 ± 5		22 ± 2	3 ± 2	0.27	14	No. 2b	7/5/79
92 ± 7		62 ± 3	23 ± 2	0.30	28	No. 2c	7/5/79

<sup>a</sup>No differentiation made between various depths of soil.

<sup>b</sup>Samples taken vary from 2 to 9 and 2 to 12-cm depth.

<sup>c</sup>Uncertainties represent two standard deviations of counting error.

<sup>d</sup>Improved radiochemical analysis resulted in a lower detection limit for samples obtained after November 10, 1978.

Table 4. Concentrations of  $^{99}\text{Tc}$  in vegetation and soils in the vicinity of Paducah Gaseous Diffusion Plant

Concentrations (Bq/kg dry wt)						Location	Date of collection
Vegetation	Soil <sup>a</sup>	Soil (0-2 cm)	Soil <sup>b</sup> (below 2 cm)	Biomass (kg dry wt/m <sup>2</sup> )	Plant inventory (Bq/m <sup>2</sup> )		
250	< 80	-	-	-	-	No. 1	7/20/78
1300	≤ 100	-	-	-	-	No. 2	7/20/78
450 ± 30 <sup>c</sup>		13 ± 1.8	9.9 ± 1.5	-	-	No. 1	10/23/78
1300 ± 50		120 ± 0.5	38 ± 3	-	-	No. 2	10/23/78
300 ± 20		62 ± 3	58 ± 3	0.506	150	No. 1a	8/21/79
480 ± 20		27 ± 3	40 ± 3	0.526	250	No. 1b	8/21/79
230 ± 20		52 ± 3	28 ± 3	0.470	110	No. 1c	8/21/79
1600 ± 30		68 ± 3	65 ± 3	0.198	320	No. 2a	8/21/79
1400 ± 30		90 ± 5	85 ± 5	0.184	260	No. 2b	8/21/79
1200 ± 30		92 ± 5	47 ± 3	0.213	260	No. 2c	8/21/79

<sup>a</sup>No differentiation made between various depths of soil.

<sup>b</sup>Samples taken vary from 2 to 7 to 2 to 10-cm depth.

<sup>c</sup>Uncertainties represent two standard deviations of counting error.

<sup>d</sup>Improved radiochemical analysis resulted in a lower detection limit for samples obtained after July 20, 1978.

Table 5. Concentrations of  $^{99}\text{Tc}$  in vegetation and soils in the vicinity of Portsmouth Gaseous Diffusion Plant

Concentrations (Bq/kg dry wt)				
Vegetation	Soil (0-2 cm)	Soil (below 2 cm) <sup>a</sup>	Location	Date of collection
< 80	$0.8 \pm 0.7^b$	$1.0 \pm 0.8$	Site A	10/31/78
< 80	$2.5 \pm 1$	$0.3 \pm 0.0$	Site B	10/31/78
$13 \pm 7$	$10 \pm 2$	$9.5 \pm 0.8$	Site 1	4/5/79
$57 \pm 20$	$3.0 \pm 1$	$5.3 \pm 1$	Site 2	4/5/79
$48 \pm 15$	$2.3 \pm 1$	$1.8 \pm 1$	Site 3	4/5/79
$17 \pm 7$	$0.73 \pm 0.80$	$1.3 \pm 0.87$	Site 4	4/5/79
$5 \pm 3$	$0.70 \pm 0.84$	$1.2 \pm 0.9$	Site 5	4/5/79
$25 \pm 11^c$	$12 \pm 7^d$	$12 \pm 5^d$	Site 25 <sup>e</sup>	9/7/79
$190 \pm 54^f$	$13 \pm 5^d$	$13 \pm 7^d$	Site 26 <sup>e</sup>	9/7/79
$32 \pm 15^f$	$9.2 \pm 5^d$	$1.7 \pm 1.7^d$	Site 29 <sup>e</sup>	9/7/79

<sup>a</sup>Samples taken from 2 to 15-cm depth.

<sup>b</sup>Uncertainties are two standard deviations of counting error.

<sup>c</sup>Average of five subsamples.

<sup>d</sup>Average of two subsamples.

<sup>e</sup>Collected by personnel of Portsmouth Gaseous Diffusion Plant inside perimeter fence.

<sup>f</sup>Average of three subsamples.

Table 6. Comparison of detected  $^{99}\text{Tc}$  concentrations in selected soils and vegetation using radiochemical analysis (RCA) and isotope dilution mass spectrometry (IDMS)

Sample location	$^{99}\text{Tc}$ concentrations (Bq/kg)					
	Grass			Soil		
	RCA	IDMS	Ratio	RCA	IDMS	Ratio
Paducah No. 2a	1600	1700	0.94	68	62	1.1
Paducah No. 2b	1400	1200	1.2	90	94	0.96
Paducah No. 1c	230	180	1.3	28	32	0.88
Portsmouth No. 26c	120 <sup>a</sup>	40 <sup>b</sup>	3.0	-	-	-
Portsmouth No. 26b	270 <sup>a</sup>	230	1.2	-	-	-

<sup>a</sup>Results of reanalysis after interferences in beta counting were eliminated; initial results were: Portsmouth No. 26a, 230 Bq/kg; Portsmouth No. 26b, 400 Bq/kg.

<sup>b</sup>Value suspected to be subject to error due to weak signal.

including the estimated values of standing crop biomass and plant  $^{99}\text{Tc}$  inventory are listed in Table 3.

### 3.1.2 Paducah Gaseous Diffusion Plant

The concentrations of  $^{99}\text{Tc}$  in vegetation sampled near the Paducah Gaseous Diffusion Plant range from 230 to 480 Bq/kg dry wt at sampling location No. 1 and from  $1.2 \times 10^3$  to  $1.6 \times 10^3$  Bq/kg dry wt at sampling location No. 2. The geometric mean value over all vegetation concentrations is 670 Bq/kg with a geometric standard deviation of 2.2. The soil concentrations range from 13 to 62 Bq/kg in the top 2-cm samples and from 9.9 to 58 Bq/kg in the below 2 cm samples taken from location No. 1. For sampling location No. 2 the soil concentrations in the top 2-cm range from 68 to 120 Bq/kg and from 38 to 85 Bq/kg in the below 2-cm samples. The geometric mean for all soil samples taken at the 0 to 2-cm depth is 54 Bq/kg with a geometric standard deviation of 2.1. The geometric mean at the below 2-cm depth for all soil samples is 40 Bq/kg with a geometric standard deviation of 1.9.

When account is taken of the estimated standing crop biomass of vegetation sampled during August 21, 1979, the concentrations (Bq/kg) of  $^{99}\text{Tc}$  in vegetation can be converted to estimates ( $\text{Bq/m}^2$ ) of an inventory of  $^{99}\text{Tc}$  in vegetation (plant  $^{99}\text{Tc}$  inventory = biomass x concentration). The geometric mean for the inventory of activity in vegetation is  $160 \text{ Bq/m}^2$  for sampling location No. 1 and  $280 \text{ Bq/m}^2$  for sampling location No. 2. The concentrations of  $^{99}\text{Tc}$  detected for each sample collected in the vicinity of the Paducah Gaseous Diffusion Plant including the estimated values of standing crop biomass and plant  $^{99}\text{Tc}$  inventory are listed in Table 4.

### 3.1.3 Portsmouth Gaseous Diffusion Plant

The concentrations of  $^{99}\text{Tc}$  in vegetation sampled near the Portsmouth Gaseous Diffusion Plant range from 5.0 to 190 Bq/kg dry wt for all sampling locations. The concentrations in the top 2 cm of soil range from 0.7 to 13 and from 0.33 to 13 Bq/kg in the below 2-cm soil samples. The geometric means and standard deviations for vegetation



and soil are: 29 Bq/kg and 3.0 for vegetation, 3.2 Bq/kg and 3.3 for soil sampled at a depth of 0-2 cm, and 2.5 Bq/kg and 3.5 for soil sampled at a depth below 2 cm. The large geometric standard deviations are influenced by the higher concentrations associated with sampling locations 25, 26, and 29 which were situated within the perimeter fence. Considering only the locations sampled outside the perimeter fence, the geometric means and standard deviations are: 20 Bq/kg and 2.7 for vegetation, 1.8 Bq/kg and 2.7 for soil (0-2 cm), and 1.7 Bq/kg and 3.1 for soil (below 2 cm). Table 5 lists the results of  $^{99}\text{Tc}$  concentrations in vegetation and soil for the Portsmouth Gaseous Diffusion Plant. No quantitative estimate of standing crop biomass was obtained for the vegetation sampled at Portsmouth.

### 3.2 Comparison of Results of Radiochemical Analysis and Isotope Dilution Mass Spectrometry

The results of a comparison of detected  $^{99}\text{Tc}$  concentrations in selected soils and vegetation using radiochemical analysis (RCA) and isotope dilution mass spectrometry (IDMS) indicate no bias associated with the RCA method, with the difference in concentrations reported by the two methods being on the order of 10% (Table 6). Because of the expense incurred with the IDMS method, the criteria used to select samples for testing were based on apparent discrepancies in results reported with the RCA method. Paducah samples were selected because concentrations appeared to be significantly larger than those reported for the other two facilities. Portsmouth samples were selected because of suspected contamination during preparation for radiochemical analysis by an unknown low-energy beta emitter.

### 3.3 Soil-to-Plant Concentration Factors

Soil-to-plant concentration factors were calculated from the concentrations in vegetation and soils by estimating a soil concentration that is indicative of a 0 to 15-cm root zone and dividing this estimated concentration into the observed concentration in vegetation for each sampling site and sampling period. Where the concentration in soil was differentiated into two depths, 0 to 2 cm and

below 2-cm, the concentration for 0 to 15 cm was estimated by multiplying the surface soil concentration by two and multiplying the lower soil concentration by 13, adding the products, and dividing by 15.

$$\text{Soil}_{0-15 \text{ cm}} = \frac{(\text{Soil}_{0-2 \text{ cm}} \times 2) + (\text{Soil}_{\text{below 2 cm}} \times 13)}{15} .$$

Soil-to-plant concentration factors derived in this manner are listed in Table 7 for each gaseous diffusion facility.

The highest values of the concentration factor are associated with Paducah. The most variability is associated with the concentration factors calculated for Portsmouth. The concentration factors estimated for the Oak Ridge Gaseous Diffusion Plant range from 3.3 to 16.0 with a geometric mean of 7.0 and a geometric standard deviation of 1.7. The range of concentration factors for Paducah is from 5.1 to 44 with a geometric mean of 16 and a geometric standard deviation of 2.0. For Portsmouth the range is from 1.4 to 26 with a geometric mean of 7.4 and a geometric standard deviation of 2.8.

A probability plot of the pooled concentration factors of all three facilities is shown in Fig. 5. This pooled assemblage of concentration factors appears to be reasonably lognormal with an overall geometric mean of 9.5 and a geometric standard deviation of 2.4. Table 8 presents a statistical summary of the pooled assemblage of <sup>99</sup>Tc soil-to-plant concentration factors.

No correlation could be ascertained between soil pH, organic matter content of soil, and the soil-to-plant concentration factor. With the exception of sites 1 and 29 at Portsmouth, which had a soil pH ranging from 4.7 to 5.7, all other sampling locations had soil pH values ranging from 6.0 to 7.3. The top 2 cm of soil generally contained about twice the organic matter (6 to 19%) as soil samples obtained below 2 cm (4 to 7%). Table 9 presents the results for those soils for which pH and organic matter content were determined.

Table 7. Soil-to-plant concentration factors (CF) for <sup>99</sup>Tc

Oak Ridge Gaseous Diffusion Plant				Paducah Gaseous Diffusion Plant			Portsmouth Gaseous Diffusion Plant		
CF (vegetation/soil)	Location	Date	CF (vegetation/soil)	Location	Date	CF (vegetation/soil)	Location	Date	CF (vegetation/soil)
10	No. 1	11/10/78	44	No. 1	10/23/78	1.4	Site 1	4/5/79	
11	No. 2	11/10/78	27	No. 2	10/23/78	11	Site 2	4/5/79	
4.7	No. 1a	7/5/79	5.1	No. 1a	8/21/79	26	Site 3	4/5/79	
4.2	No. 1b	7/5/79	13	No. 1b	8/21/79	14	Site 4	4/5/79	
16.0	No. 1c	7/5/79	7.4	No. 1c	8/21/79	4.4	Site 5	4/5/79	
5.5	No. 2a	7/5/79	24	No. 2a	8/21/79	2.1	Site 25	9/7/79	
9.4	No. 2b	7/5/79	16	No. 2b	8/21/79	15	Site 26	9/7/79	
3.3	No. 2c	7/5/79	23	No. 2c	8/21/79	12	Site 29	9/7/79	
Geometric mean 7.0			Geometric mean 16			Geometric mean 7.4			
Geometric S.D. 1.7			Geometric S.D. 2.0			Geometric S.D. 2.8			

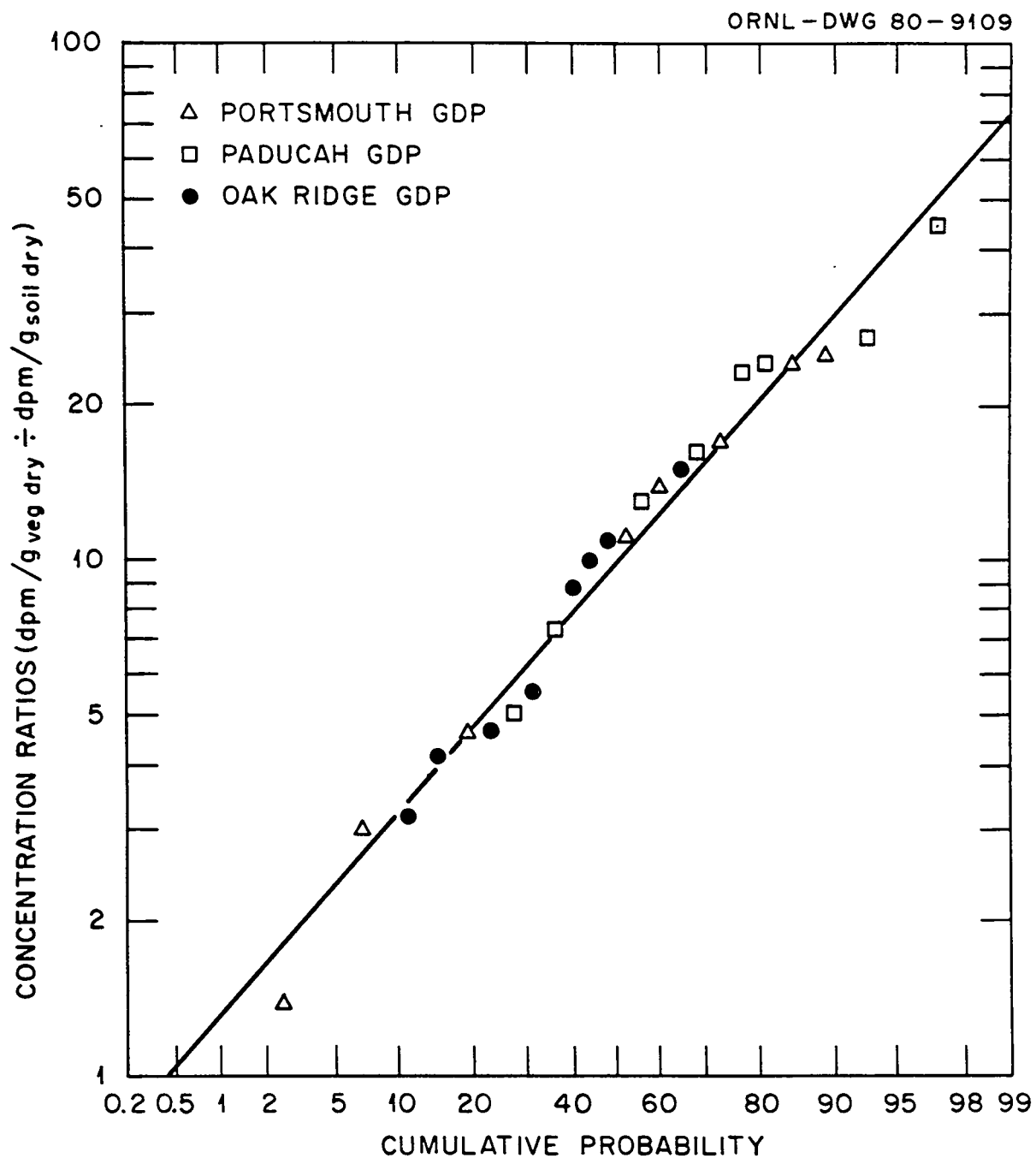


Fig. 5. Lognormal probability plot of soil-to-plant concentration factors pooled from all three gaseous diffusion facilities.

#### 4. CONCLUSIONS

##### 4.1 Feasibility of Measuring Technetium-99 in Vegetation and Soils

The radiochemical method that incorporates low-background beta counting is a reliable method for determining  $^{99}\text{Tc}$  in environmental (soil and vegetation) materials. Concentrations of a few Becquerals (Bq) per kilogram of soil and/or vegetation (corresponding to a detection limit of 0.03 Bq) have been measured in environmental samples by this method. Several samples of varying concentrations were selected from a large group to be analyzed by isotope dilution mass spectrometry (IDMS) for comparison of the two methods and for verification of the results (Table 6). All except two of the results from the two methods compared favorably. In the two cases of poor agreement, contamination during sample preparation for radiochemical analysis by unidentified activity was suspected. The interferences caused by this suspected contamination were detected by counting with Al absorbers, a practice used to verify purity of the separated Tc. The fact that the absorber counts did detect interferences adds credibility to the method. Because of these interferences, the two samples were reanalyzed. The results of the reanalysis produced lower values of activity concentration, but one value was still significantly higher than the value obtained with the IDMS method. In this case, error is suspected in the IDMS value due to the presence of a very weak signal.

The practice of taking duplicates, with one of the duplicates being spiked with  $^{95\text{m}}\text{Tc}$ , is a very practical approach in determining  $^{99}\text{Tc}$ , because this practice allows one to utilize either the beta-counting method or the IDMS method for final measurements. Should the concentration of  $^{99}\text{Tc}$  in a sample be too low for satisfactory results from the beta-counting method, it is a simple operation to subsequently add  $^{97}\text{Tc}$  as a spike and perform IDMS analysis. This practice not only saves time by eliminating the need to start the analysis anew but it is also economical in the use of  $^{97}\text{Tc}$  tracer, which is rather expensive.

Table 8. Statistical summary of soil-to-plant concentration factors combined from all sampling sites

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Number of values	24
Maximum value (Paducah)	44
Minimum value (Portsmouth)	1.4
Arithmetic mean	14
Standard deviation	10
Standard error	2.0
Geometric mean <sup>a</sup>	9.5
Geometric standard deviation <sup>b</sup>	2.4
Geometric standard error <sup>c</sup>	1.2

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<sup>a</sup>Geometric mean = exponential of the mean of logtransformed data.

<sup>b</sup>Geometric standard deviation = exponential of the standard deviation of logtransformed data.

<sup>c</sup>Geometric standard error = exponential of the standard error of logtransformed data.

Table 9. Summary of pH and organic matter (OM) content of soils sampled in the vicinity of gaseous diffusion facilities

Facility	Soil location	Soil depth			
		(0-2 cm)		(below 2 cm)	
		pH	% OM	pH	% OM
Oak Ridge	No. 1a	6.4	11.7	6.8	5.5
	No. 1b	6.2	7.7	7.0	6.1
	No. 1c	7.0	8.5	6.9	6.3
	No. 2a	6.5	15.3	6.9	6.8
	No. 2b	6.8	16.4	7.1	6.8
	No. 2c	6.7	18.8	7.1	6.3
Paducah	No. 1a	6.6	7.5	6.6	5.5
	No. 1b	6.5	13.2	6.8	7.3
	No. 1c	6.0	14.2	6.6	5.9
	No. 2a	6.9	7.3	6.7	5.5
	No. 2b	6.4	7.2	7.0	4.5
	No. 2c	7.1	10.0	7.1	6.0
Portsmouth	Site 25	6.8	10.0	6.6	6.4
	Site 26	6.8	7.3	6.5	4.9
	Site 29	5.5	5.6	4.9	4.0
	Site 1	5.2	a	5.0	a
	Site 2	7.0		7.0	
	Site 3	6.8		6.9	
	Site 4	6.3		7.0	
	Site 5	6.8		7.3	

<sup>a</sup>Organic matter content not determined for remaining sites.

## 4.2 Significance of Soil-to-Vegetation Concentration Factors in Radiological Assessments

### 4.2.1 A Comparison of Concentration Factors

A comparison of the soil-to-plant concentration factors for  $^{99}\text{Tc}$  obtained from laboratory experiments (Tables 1 and 2) with the concentration factors from field measurements in the vicinity of the three operating gaseous diffusion plants (Tables 7 and 8) reveals that the laboratory values are greater than field values by one to two orders of magnitude. The geometric mean of 9.5 for the field data is about 20 times less than the value of 200 assumed in the radiological assessment performed by Till et al. (1979). Soil-to-plant concentration factors that would be representative of a chronic release of  $^{99}\text{Tc}$  have been estimated from field experiments in which a spike of  $^{95\text{m}}\text{TcO}_4^-$  was applied as a tracer (Hoffman et al. in preparation). Concentration factors were calculated from these experiments by using values of the initial concentration in soil and vegetation and the respective loss rates, correcting for the differences in the radiological decay constants of  $^{95\text{m}}\text{Tc}$  (half-life of 61 d) and  $^{99}\text{Tc}$  (half-life of  $2.1 \times 10^5$  years).

A concentration factor of 22 was estimated from the series of field experiments in which both soil and mixed herbaceous vegetation (dominated by Festuca sp. and Lespedeza sp.) were contaminated through direct application of  $^{95\text{m}}\text{Tc}$ . A concentration factor of 6.7 was estimated from the series of field experiments in which the concentration of  $^{95\text{m}}\text{Tc}$  in vegetation was entirely due to uptake from contaminated soil. These values are comparable to the concentration factors derived from soil and vegetation measurement in the vicinity of the Oak Ridge, Portsmouth, and Paducah Gaseous Diffusion Plants.

There are several plausible explanations as to why an apparent discrepancy exists between laboratory and field data. In laboratory experiments with potted plants a greater ratio of root-to-soil volume may exist, thus enhancing the capacity for root uptake of technetium. Artificially enhanced aeration of the soils in pot experiments may also occur during preparation of the soil prior to sowing with seeds.



Enhanced aeration could inhibit the capacity of the soil to reduce the technetium to less soluble chemical compounds. Laboratory pot experiments also are conducted so as to protect vegetation from conditions occurring in the field such as wind, fog, and rain. These conditions could contribute to the removal of technetium from vegetative tissue. Two laboratory studies report a decline in the soil-to-plant concentration factor with time (Routson and Cataldo 1978, Cataldo 1979). In these studies, reduction of Tc to the IV valence state is mentioned as a possible mechanism which decreases the availability of Tc in soil. Landa et al. (1977) and Gast et al. (1979) also report an increase in the sorption of  $^{99}\text{TcO}_4^-$  by soils with time. Their experiment suggest increased sorption might be due to the role of the living organic fraction of soil. Anaerobic conditions did not appear to be a prerequisite for  $^{99}\text{Tc}$  soil sorption. Our field studies with  $^{95\text{m}}\text{Tc}$  support the presence of mechanisms which remove technetium from the vegetation and chemically reduce soluble forms of technetium ( $\text{TcO}_4^-$ ) in the soil.

Another possible explanation for the discrepancy between laboratory and field data is that the concentrations of  $^{99}\text{Tc}$  applied in some potted plant experiments are so high that the ferrous ion and organic matter content of the soil is not sufficient to reduce and/or sorb a significant fraction of the applied technetium. At concentrations typical of what would prevail in the environment following routine discharges, the available ferrous ions and organic matter might be more effective in reducing or sorbing the chemical form of the applied Tc. The soil concentrations in the experiments performed by Gast et al. (1976) were on the order of  $1\text{ }\mu\text{g/g}$ . The soil concentrations in the experiments performed by Wildung et al. (1977) ranged from  $0.001$  to  $5\text{ }\mu\text{g/g}$ . The concentrations in soil taken from the vicinity of the three operating gaseous diffusion facilities ranged from approximately  $5 \times 10^{-7}$  to  $2 \times 10^{-4}\text{ }\mu\text{g/g}$  ( $1\text{ Bq/kg} = 1.6 \times 10^{-6}\text{ }\mu\text{g/g}$  for  $^{99}\text{Tc}$ ), and the concentrations of  $^{95\text{m}}\text{Tc}$  applied in the field experiments ranged from  $2 \times 10^{-8}$  to  $2 \times 10^{-9}\text{ }\mu\text{g/g}$  soil.

Although the field experiment involved different vegetation species than were used in the laboratory experiments, soil-to-plant concentration factors from all laboratory species are consistently larger than concentration factors observed in the field. For example, the largest soil-to-plant concentration factor observed at the termination of our field experiment using  $^{95m}\text{TcO}_4^-$  was 10, which was the value associated with panic grass (Panicum sp.). The lowest concentration factor observed at the end of these experiments was 0.5, associated with Johnson grass (Sorghum halepense). These observed values, however, are not directly related to the steady state values of 22 and 6.7, as the steady state values were calculated using information on the dynamic behavior of technetium among all species in the field.

All of the above reasons for the observed discrepancy between the results obtained from potted plant experiments and field studies are speculative. Further research will be needed to test these suggested explanations and to identify which of these explanations contribute most significantly to the differences in results.

#### 4.2.2 Consideration of Removal Mechanisms of Technetium-99 from Vegetation and Soils

As discussed above, soil-to-vegetation concentration factors obtained under field conditions are approximately one to two orders of magnitude less than those obtained in the laboratory. One of the speculated reasons is that in the field, processes such as leaching could be effectively removing quantities of  $^{99}\text{Tc}$  in vegetation and in the root zone of soil. A decrease of activity with time was observed in our field experiments in which vegetation and soil were spiked with a spray of a solution containing  $^{95m}\text{TcO}_4^-$  (Hoffman et al. in preparation). The effective half-lives (correcting for radioactive decay) were approximately 16 to 40 d for vegetation and 200 to 300 d for the 0- to 15-cm depth of soil. Thus, not only does this information indicate that the soil-to-plant concentration factor is time dependent, but also that accumulation of a chronic deposit of

$^{99}\text{Tc}$  in soil should no longer be assumed to increase linearly with time periods of 15 to 100 years as is currently assumed in radiological assessment models (USNRC 1977, Till et al. 1979, Moore et al. 1979). The effective half-lives for vegetation reflect the combined effect of several processes including: leaching from vegetation, uptake from soil, leaching from soil, reduction of technetium in soil to a biologically less available chemical form, and dilution of activity as the result of increasing biomass with vegetation growth. The consideration of these effects in assessment models would result in the estimated  $^{99}\text{Tc}$  concentrations in vegetation being much less than if adjustments are made only to account for differences in laboratory and field-derived soil-to-plant concentration factors (Hoffman et al., in preparation). Soil-to-plant concentration factors derived from measurements made in the vicinity of the three gaseous diffusion facilities are comparable to the equilibrium concentration factors calculated from field experiments where loss rates of  $^{95\text{m}}\text{Tc}$  were observed in soil and vegetation subsequent to a spike application of  $^{95\text{m}}\text{TcO}_4^-$ . The prevalence of mechanisms removing technetium from soil and vegetation in the vicinity of these facilities remains to be confirmed through further research.

#### 4.2.3 The Estimated Consequence of a Hypothetical 1 Ci per Year ( $3.7 \times 10^{10}$ Bq/year) Release Rate

An estimation of the radiological significance of the results in this report is made by using an approach similar to that of Till et al. (1979). This was the approach used to initially identify that  $^{99}\text{Tc}$  releases from uranium enrichment facilities could be of potential radiological importance as a consequence of the high soil-to-plant concentration factors derived from laboratory experiments. Assuming a release height of 20 m and a receptor located 1600 m downwind of the facility, Till et al. (1979) calculated an annual average air concentration 1 m above ground of  $1.2 \times 10^{-3} \text{ Bq/m}^3$ . This air concentration corresponds to a deposition rate of  $1.1 \text{ Bq m}^{-2} \text{ d}^{-1}$  resulting from both wet- and dry-deposition processes.

Using the terrestrial food chain transport model of NRC Regulatory Guide 1.109 (NRC 1977), approximately 7 Bq/kg\* in vegetation was calculated due to direct deposition, and approximately 5000 Bq/kg\* in vegetation was calculated as the result of uptake from the soil and an assumed soil-to-plant concentration factor of 200.\* The soil, with a concentration of 25 Bq/kg, was assumed to have received activity for 15 continuous years with no losses other than radiological decay. The organ doses to a hypothetical human receptor consuming a daily quantity of 175 g (fresh weight) of vegetables, 300 g of meat and 0.3 liters of milk was 18 mrem ( $1.8 \times 10^{-4}$  Sv) to the G. I. tract and 80 mrem ( $8.0 \times 10^{-4}$  Sv) to the thyroid gland.

A soil-to-vegetation concentration factor of 10 instead of 200 would reduce the above dose estimates by a factor of 20. The revised organ doses would be 0.9 and 4 mrem, respectively. The corresponding vegetation concentration would be 250 Bq/kg. The concentration factor of 10 approximates the geometric mean of soil-to-plant concentration factors derived from soil and vegetation measurements obtained around the three gaseous diffusion facilities. This concentration factor of 10 is also comparable to calculated concentration factors obtained using data from field experiments on the dynamics of  $^{95m}\text{TcO}_4^-$  in soil and plants (Hoffman et al., in preparation). However, if the environmental half-time of 16-d observed in these experiments is relevant as a net of the processes of growth dilution, leaching of materials deposited on the surfaces and incorporated within the tissue of vegetation, leaching from soil, uptake from soil, and chemical reduction of the Tc in soil, then the calculated vegetation concentration and resulting hypothetical doses should be lower by more than just a factor of 20.

A fractional interception by herbaceous vegetation of about  $1.1 \text{ m}^2/\text{kg}$  (concentration per kg vegetation / concentration per  $\text{m}^2$ )

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\*These values have been converted from wet to dry weight concentrations assuming vegetation to be 25% dry matter.

deposit) was measured in the field experiments using  $^{95m}\text{TcO}_4^-$ . This value combined with the 16-d environmental half-time and a continuous deposition rate of  $1.1 \text{ Bq m}^{-2} \text{ d}^{-1}$  results in a calculated vegetation concentration at equilibrium of 28 Bq/kg dry matter,

$$\begin{aligned} C_v &= d \times F \times T_w / \ln 2 \\ &= (1.1 \text{ Bq m}^{-2} \text{ d}^{-1}) (1.1 \text{ m}^2/\text{kg}) (16 \text{ d} / \ln 2) \\ &= 28 \text{ Bq/kg} , \end{aligned}$$

where

- $C_v$  is the concentration in vegetation at equilibrium,
- $d$  is the deposition rate ( $\text{Bq m}^{-2} \text{ d}^{-1}$ ),
- $F$  is the fraction of an area deposit intercepted per mass vegetation ( $\text{m}^2/\text{kg}$ ), and
- $T_w$  is the net environmental half-time resulting from removal of Tc from vegetation and soil and vegetation uptake of Tc from soil (d).

This concentration would correspond to calculated doses of 0.1 mrem ( $1 \times 10^{-6} \text{ Sv}$ ) to the G. I. tract and 0.45 mrem ( $4.5 \times 10^{-6} \text{ Sv}$ ) to the thyroid gland using the same assumptions for dietary habits and internal  $^{99}\text{Tc}$  dosimetry as used by Till et al. (1979). Therefore, if research can confirm the prevalence of a net environmental half-time for  $^{99}\text{Tc}$  taken up by vegetation, the estimated radiological impact will be reduced substantially.

Before a valid comparison can be made between the above calculated vegetation concentrations and measured concentrations in vegetation obtained in the vicinity of the three gaseous diffusion plants, detailed information on the characteristics of the release rates and meteorological conditions prevailing at each site will be necessary. It is interesting to note, however, for the sake of comparison, that the highest single concentration observed in vegetation, a sample collected at sampling location No. 2a just outside the perimeter fence

of Paducah Gaseous Diffusion Plant, is still a factor of three below the 5000 Bq/kg vegetation concentrations predicted by Till et al. (1979). On the average, the observed vegetation concentrations for the Oak Ridge Gaseous Diffusion Plant and the Portsmouth Gaseous Diffusion Plant are factors of 68 and 150, respectively, below the concentrations predicted by Till et al. The Paducah plant is associated with average vegetation concentrations about 7.5 times below the concentrations predicted by Till et al. Although the differences between the vegetation concentrations observed in the vicinity of the three gaseous diffusion plants cannot at this time be fully explained, some influence may be accounted for by variations in release rate, distances from the release, and micrometeorological effects such as building wakes.

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## 6. APPENDICES

### Appendix A: Procedures for Radiochemical Analysis of Technetium-99 in Environmental Samples

#### 1.0 Scope and Application

- 1.1 This method is applicable to the determination of  $^{99}\text{Tc}$  in soil, sediment, and vegetation samples.
- 1.2 The lowest concentration reported by beta counting is 0.001 Bq/g when analyzing 25 g of sample, counting for one hour on a beta counter with a 0.6 cpm background and a 25% efficiency, and realizing a 75% chemical recovery. This corresponds to a limit of detection of 0.03 Bq.
- 1.3 The limit of detection by isotope dilution mass spectrometry is 0.0006 Bq or 1 pg of  $^{99}\text{Tc}$ .

#### 2.0 Summary of Method

- 2.1 Soil samples are leached with  $\text{NaOCl}$  and  $\text{H}_2\text{O}_2$  prior to radiochemical separation; vegetation samples are ashed and fused with  $\text{K}_2\text{CO}_3$ ; then the fused samples are dissolved in  $\text{H}_2\text{O}$ .
- 2.2 Following the preparation, the samples are extracted with methyl ethyl ketone, dissolved in  $\text{H}_2\text{O}$ , scavenged by hydroxide precipitation, and recycled through the methyl ethyl ketone extraction. The final water strip is either dried on stainless steel discs for beta counting or adsorbed on anion resin beads in preparation for isotope dilution mass spectrometry analysis (IDMS).

#### 3.0 Sample Handling and Preservation

- 3.1 Soil samples are oven-dried at  $105^\circ\text{C}$ , milled, and sieved through a 100-mesh screen.
- 3.2 Vegetation samples are oven-dried at  $105^\circ\text{C}$  and milled.
- 3.3 Both materials are stored in either plastic or glass containers.

#### 4.0 Interferences

- 4.1 Any beta-emitting radionuclide that is not thoroughly removed by the chemical separation steps will interfere with the beta-counting technique. Counting with an Al absorber with the half-thickness ( $7.2 \text{ mg/cm}^2$ ) appropriate for  $^{99}\text{Tc}$  can be used to detect most of this type of interference.
- 4.2 Several elements, such as Ru and Mo, can interfere in the IDMS analysis (see method for IDMS in Appendic).

#### 5.0 Reagents

- 5.1 Sodium hypochlorite, 6% NaOCl.
- 5.2 Hydrogen peroxide, 30%  $\text{H}_2\text{O}_2$ .
- 5.3 Ammonium hydroxide, Conc.  $\text{NH}_4\text{OH}$ .
- 5.4 Sodium hydroxide, 50% w/w NaOH.
- 5.5 Methyl ethyl ketone (MEK).
- 5.6 Anion exchange resin, Dowex 1-X4.
- 5.7 Iron holdback carrier, 0.1 M  $\text{Fe}(\text{NO}_3)_3$ .
- 5.8 Technetium-95m tracer, 1 to  $10 \times 10^4$  cpm/ml.
- 5.9 Technetium-97, 10 ng/ml.
- 5.10 Technetium-99, standardized solution.

#### 6.0 Apparatus

- 6.1 Balance.
- 6.2 Centrifuge.
- 6.3 Labware.
  - 6.3.1 Beakers, 500-ml tall-form, 250-ml, and 100-ml.
  - 6.3.2 Centrifuge tubes and bottles, 50-ml and 250-ml glass.
  - 6.3.3 Separatory funnels, 250, and 60-ml.
- 6.4 Pasteur pipets.
- 6.5 Hot plate.
- 6.6 Multichannel pulse-height analyzer with NaI(Tl) detector.
- 6.7 Low-background beta counter.
- 6.8 Stainless steel discs, sized to fit counter.
- 6.9 Serum vials, 400 ml.

## 7.0 Procedure for Soil Preparation

- 7.1 Transfer 100 g of soil that has been dried, milled, and sieved to a 500-ml tall-form beaker and slowly add 150 ml of 6% NaOCl.
- 7.2 Digest at 80 to 90°C for 1 h with stirring.
- 7.3 Transfer the sample to a 250-ml centrifuge bottle and centrifuge at 2000 rpm for 15 to 20 min.
- 7.4 Decant the supernate into a 1000-ml beaker.
- 7.5 Add 150 ml of NaOCl to the 150-ml centrifuge bottle and stir to suspend the soil.
- 7.6 Centrifuge at 2000 rpm for 15 min.
- 7.7 Add the supernate to the first leach solution in the 1000-ml beaker and discard the soil.
- 7.8 Add 30% H<sub>2</sub>O<sub>2</sub> to the solution in 1-ml increments and heat to boiling until the solution clears and the volume is reduced to 75 ml. Cool and transfer by filtering to a 200-ml volumetric flask, then dilute to the 200-ml mark with water.
- 7.9 Transfer measured aliquots to 250-ml separatory funnels.
- 7.10 Add 10000 cpm (gamma) of <sup>95m</sup>Tc and/or 1 ng of <sup>97</sup>Tc to one of the aliquots.

## 8.0 Procedure for Vegetation Preparation

- 8.1 Transfer known weights of the dried and milled vegetation (25-50 g) to one-liter plastic bags (duplicates).
- 8.2 Add enough NH<sub>4</sub>OH to thoroughly wet the vegetation.
- 8.3 Add <sup>95m</sup>Tc and/or <sup>97</sup>Tc as in step 7.10 to one of the duplicates.
- 8.4 Knead the wet vegetation in the plastic bag until all of the material is thoroughly saturated.
- 8.5 Place the bag containing the sample in a 500-ml tall-form beaker.
- 8.6 Place the beaker in a drying oven at 105°C and take to dryness.

- 8.7 Move the beaker and contents to a muffle furnace set at 250°C and thoroughly char the material (2-4 h).
- 8.8 Raise the temperature of the furnace to 500°C and allow the sample to ash for 8 to 16 h.
- 8.9 Transfer the ashed material to a 100-ml platinum dish.
- 8.10 Add 8 g of  $K_2CO_3$  for every 20 g of original dry sample.
- 8.11 Fuse over a flame until a fluid melt appears.
- 8.12 Cool and dissolve the fused material in approximately 20 ml of  $H_2O$ .
- 8.13 Transfer the dissolved sample to a 50-ml centrifuge tube and centrifuge at 2000 rpm for 15 min.
- 8.14 Decant the supernate into a 250-ml separatory funnel and discard any solids that remain.

#### 9.0 Separation Procedure

- 9.1 Adjust the sample solution in the separatory funnel to 2M in  $OH^-$ .
- 9.2 Add an equal volume of MEK.
- 9.3 Extract (either by hand or automatic shaker) for 10 min.
- 9.4 Drain the aqueous phase into a new separatory funnel and save the MEK.
- 9.5 To the aqueous phase, repeat steps 9.2 and 9.3.
- 9.6 Discard the aqueous phase and combine the MEK extracts in a 250-ml beaker.
- 9.7 Add 5 ml of  $H_2O$  to the beaker and allow the MEK to evaporate (overnight when possible).
- 9.8 Transfer the  $H_2O$  to a 50-ml centrifuge tube, add 1 drop of conc. HCl and 3 drops of 30%  $H_2O_2$ , rinse the beaker with 5 ml of  $H_2O$  and add to the tube, then add 5 drops of 0.1 M  $Fe(NO_3)_3$  solution.
- 9.9 Add 2 ml of 50% NaOH and stir well.
- 9.10 Centrifuge at 2000 rpm for 10 min.
- 9.11 Transfer the supernate to a 60-ml separatory funnel.

- 9.12 Wash the precipitate with 5 ml of H<sub>2</sub>O and repeat steps 9.10 and 9.11.
- 9.13 Add an equal volume of MEK and extract for 10 min.
- 9.14 Drain the aqueous phase into a new 60-ml separatory funnel and save the MEK.
- 9.15 Repeat step 9.13 on the aqueous phase.
- 9.16 Discard the aqueous phase and combine the MEK extracts in a 100-ml beaker.
- 9.17 Add 1 ml of H<sub>2</sub>O and allow the MEK to evaporate.

#### 10. Beta Measurements

- 10.1 Transfer the water from step 9.17 (on the portion without spikes) to a stainless steel disc and gently take to dryness on a hot plate set at 50°C.
- 10.2 Mount the stainless steel disc for beta counting and count on a low-background beta counter.

#### 11.0 Yield Determination

- 11.1 Count the spiked portion and an aliquot of the <sup>95m</sup>Tc tracer in like manners on a gamma-ray spectrometer. Ratio the counts of the spiked portion to the tracer aliquot.

#### 12.0 Efficiency Determination

- 12.1 Dry a known amount (about 100 dps) of <sup>99</sup>Tc standard on a stainless steel disc and mount in the same manner as for samples.
- 12.2 Count the standard on the low-background beta counter.
- 12.3 Calculate the efficiency as follows:

$$E = C_T/D \quad ,$$

where:

$C_T$  = net counts (cps) of the <sup>99</sup>Tc standard, and  
 $D$  = disintegration rate of the <sup>99</sup>Tc standard (dps).

### 13.0 Preparation for IDMS Analysis

- 13.1 Reduce the volume of the H<sub>2</sub>O from step 9.17 (on the portion with spikes) to 200  $\mu$ l by gentle evaporation.
- 13.2 Transfer the H<sub>2</sub>O to a 400- $\mu$ l serum vial that contains two 300- $\mu$ m-diameter resin beads.
- 13.3 Cap the vial and place on a vortex mixer for 2 h.
- 13.4 Using a Pasteur pipet, transfer the beads to a glass vial for submission for IDMS.

### 14.0 Calculations (Beta Counting)

$$^{99}\text{Tc, dps/g} = C_s / EVY \quad ,$$

where:

- $C_s$  = net counts (cps) of sample,
- $E$  = efficiency for  $^{99}\text{Tc}$  from step 12.3,
- $V$  = weight of sample (g), and
- $Y$  = chemical yield from step 11.1.

### 15.0 Precision

- 15.1 The precision is estimated to be  $\pm 20\%$ .



## Appendix B: Extraction and Separation of Technetium from Soil

An extraction procedure for determining  $^{99}\text{Tc}$  was developed. A 65-g sample of air-dried soil from a field site that had been previously spiked with  $^{95\text{m}}\text{Tc}$  was leached with 100 ml of 5%  $\text{NaOCl}$ . After heating near  $90^\circ\text{C}$  for approximately 10 min, or until no further reaction was noted, the aqueous phase was separated by centrifugation. The bleach treatment was then repeated. After the second centrifugation, the pellet was washed in 0.01 M  $\text{NaHCO}_3$  (to maintain ionic strength). The supernates were combined and evaporated to about 100 ml. Two successive treatments with 10 ml 30%  $\text{H}_2\text{O}_2$  were then accomplished near the boiling point. After the sample had evaporated to about 75 ml, the liquid was filtered through Whatman #1 filter paper. The beaker was rinsed and the rinse used to wash the filter paper. This was repeated until 100 ml was collected volumetrically. After mixing, two 10-ml aliquots were taken and counted for  $^{95\text{m}}\text{Tc}$ . The initial soil concentration was determined by replicate counting of 10 g portions in the same geometry as the 10-ml liquid samples. Results showed that  $97 \pm 2\%$  of the  $^{95\text{m}}\text{Tc}$  in the soil was removed by the  $\text{NaOCl-H}_2\text{O}_2$  leaching procedure. The  $^{95\text{m}}\text{Tc}$  was applied to the soil more than 200 d prior to extraction.



### Appendix C: Isotope Dilution Mass Spectrometry

An isotope dilution mass spectrometric technique recently developed at ORNL was used for the analysis of  $^{99}\text{Tc}$  (Anderson and Walker, 1980). After spiking with  $^{97}\text{Tc}$ , the Tc from sample and spike is isolated by chemical means and concentrated on a pair of anion exchange resin beads. Each resin bead makes a filament loading for the mass spectrometer. Filaments for this work were made from zone-refined rhenium. They were of the single V-shaped design and were prebaked in an auxiliary vacuum system for at least 30 min at  $2000^{\circ}\text{C}$  to remove impurities and reduce molybdenum background. Determination of as little as 1 pg of  $^{99}\text{Tc}$  has been achieved from the enhanced ionization afforded by the resin bead.

Application of the isotope dilution technique requires the use of thermal emission mass spectrometers equipped with pulse-counting capability for increased ion detection sensitivity. The mass spectrometer used in this work was a single focusing tandem-magnet type (Smith 1978). The instrument has a 30-cm radius and  $90^{\circ}$  deflection in each magnet. The detector is a 14-stage multiplier with a gain of  $10^6$  in the pulse-counting mode. Data are stored and processed in a PDP-11/34 computer.

The most troublesome interferences in Tc analysis are from molybdenum and ruthenium. Molybdenum from the rhenium filament interferes at  $^{97}\text{Tc}$  mass position and ruthenium, if not separated in the sample preparation procedure, interferes at  $^{99}\text{Tc}$  mass position. The interference from these elements can be corrected out by scanning mass positions of Mo and Ru which are free of isobars from other elements, namely,  $^{95}\text{Mo}$  and  $^{101}\text{Ru}$ . In each case, the correction can be made within an error of 2 to 3% if the Tc ion signal equals or exceeds the interference signal. For correction, the natural ratio of the isotopes of Mo and Ru must be assumed.



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